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R&D Trends in High Efficiency Thermoelectric Conversion Materials for Waste Heat Recovery

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1 Introduction

Fossil fuel utilization efficiency has virtually reached its limits. Therefore, use of waste heat energy is the only means of achieving further increases in energy use efficiency with this type of fuel. Because this means that a resource which had essentially been discarded will now be used, in effect, the total efficiency of the energy system using fossil fuel will be improved, even if the efficiency of the thermoelectric conversion system is not particularly high. Moreover, even assuming that the efficiency of the thermal energy system is low, the fact that waste heat is converted to electrical energy, which can be flexibly used, will have an important significance.

Development of materials which convert thermal energy to electrical energy with high efficiency (thermoelectric conversion materials) is being promoting using technologies that can realistically be applied. To date, however, the results of materials technologies and systems technologies have not reached a level that can support a thermoelectric power generation market, including cost competitiveness with other power generating systems.

This paper discusses the reasons why high efficiency thermoelectric power generation will be increasingly expected in the future from the viewpoint of various energy systems, the amount of unused waste heat, and a low carbon society based on effective utilization of thermoelectric generating systems, and introduces the thermoelectric conversion materials/manufacturing processes and the conditions for penetration of thermoelectric power generating systems. First, an outline of the thermoelectric conversion materials which have been the object of research and development to date is presented from the viewpoint of generating performance, and the thermoelectric conversion materials which should be the focus of priority in future R&D from the viewpoints of resource supplies and low environmental impact are recommended. Following this, the current status of R&D on innovative thermoelectric conversion materials by nanostructural control is described, and recommendations are offered as to how to proceed with R&D on these materials in the future.

2 Thermoelectric power generation: a long-awaited technology

2-1 *Various energy systems and recovery of unused waste heat*

Figure 1 shows the relationship between the temperature of the waste heat and the annual amount of waste heat in various types of social systems.[1,2] Because the temperature of the waste heat generated by large-scale power generating systems, steel industry furnaces, and waste incinerators is 200-300°C or higher, progress

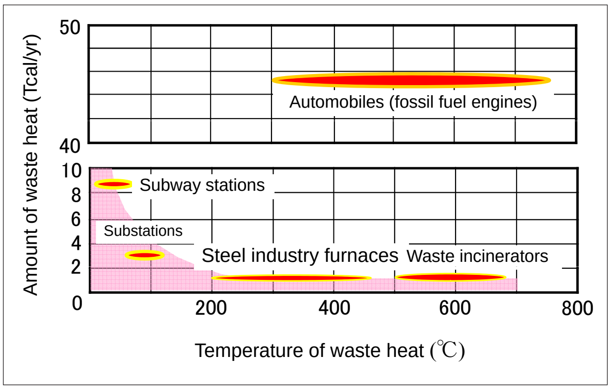

Figure 1 : Temperature and annual amount of waste heat generated by various social systems in Japan

Prepared by the STFC based on Referemces[1,2] in waste heat recovery is continuing. However, it still cannot be said that the recovery level is adequate. On the other hand, a vast amount of waste heat with temperatures of 150° or lower is generated each year by power substations, subway stations, and the like. If it is possible to establish technologies for recovering the waste heat in this low temperature region in effective energy in the future, this will contribute to a substantial reduction in energy consumption in the social system as a whole. For example, the annual waste heat generated by automobiles is estimated at 45.8Tcal,[2] and virtually all of this waste heat is discharged from engines using fossil fuels. Concretely, this is discharged in the exhaust system from the exhaust manifold immediately after the engine combustion chambers to the muffler in the latter part of the system (temperature of discharged gas: 300-700°C).

Figure 2 shows the current efficiency of various power generating systems in Japan[3] and the improvement in efficiency assuming use of thermoelectric generating systems (efficiency: 20%). Worldwide, 90% of large-scale power generating systems employ thermal power generation. Using combustion of fossil fuels as a heat source, generating efficiency is 40-60% (in combined cycle power generation using a gas turbine and steam turbine), which means that 40-60% of the heat of combustion of the fossil fuels (equivalent to approximately 15TW) is waste heat. This does not mean that all of this waste heat is simply discharged into the atmosphere without use; part of this heat is used in maintenance and control of the power generating system and as a heat source for hot water, heating, etc. Nevertheless, the amount of thermal energy which is discarded without use is quite large. If these forms of unused waste heat energy can be recovered effectively, an increase in the total efficiency of these power generating systems can be expected. In the case of automobiles with reciprocating engine drive using fossil fuels, represented by heat engines, the energy consumed for power is on the order of 30% of the energy possessed by the fuel. The amount of waste heat energy which is discarded as high temperature exhaust gas also reaches approximately 30%.

2-2 Low carbon society based on effective utilization of thermoelectric power generating systems

The establishment of technologies which recovery waste heat as effective energy will contribute to reducing the energy consumption of the social system as a whole, and thus can contribute not only to solving future energy problems, but also to solving environmental problems such as global warming. Figure 3 shows a trial calculation of

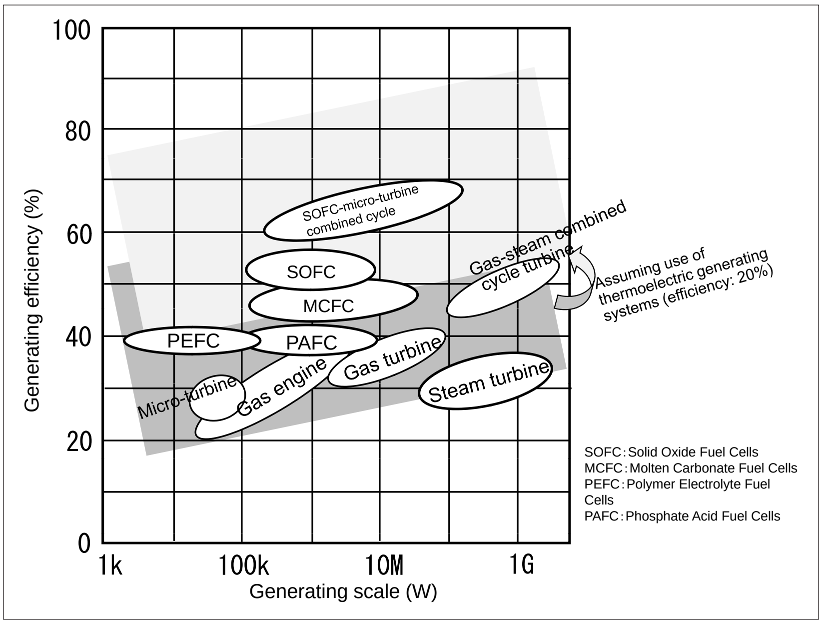

Figure 2 : Efficiency of current power generating systems and improvement of generating efficiency assuming use of thermoelectric generating systems (efficiency: 20%)

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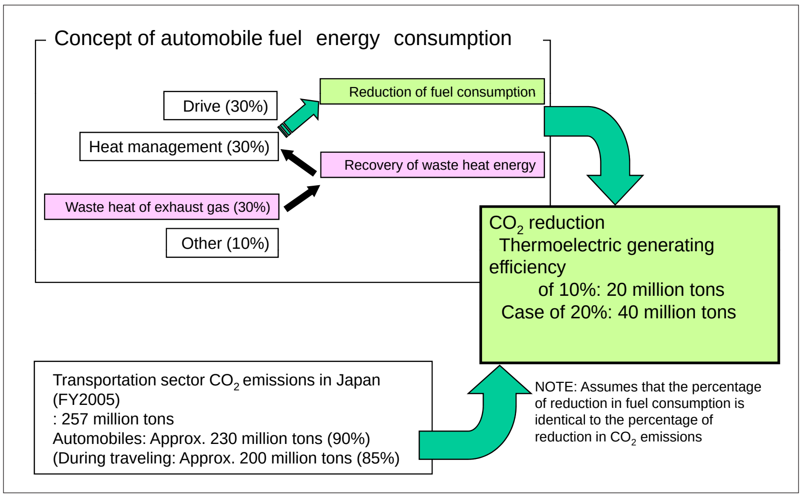

(Data from Reference[4] were used for transportation sector CO_2 emissions in Japan in FY2005.)

Figure 3 : Trial calculation of CO_2 reduction effect in case of thermoelectric power generation using waste heat energy of automotive exhaust gas

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the CO_2 reduction effect in case of thermoelectric power generation using the waste heat energy of exhaust gas in automobiles.

Transportation sector CO_2 emissions in Japan in fiscal year 2005 were approximately 257 million tons, of which, automobiles accounted for 230 million tons, or approximately 90%.[4] Assuming the largest part of these CO_2 emissions are generated during travel of automobiles with fossil fuel-burning engines, CO_2 emissions during travel account for approximately 85% of the total CO_2 emissions in the complete life cycle of the automobile.[5] From this, the CO_2 emissions attributable to total automobile travel in Japan can be estimated at approximately 200 million tons. Fuel consumption can be reduced by converting the waste heat energy of the exhaust gas to electrical energy by a thermoelectric power generating system and reusing this energy. In simple terms, assuming that thermoelectric power generating efficiency and the percentage of reduction in fuel consumption are identical with the percentage of reduction in CO_2 emissions, it is possible to reduce CO_2 by 40 million tons per year by introducing thermoelectric power generating systems with efficiency of 20%. Approximately 50% of Japan's annual greenhouse gas reduction target (CO_2 conversion) could be achieved by this method.

At present, the Ministry of Economy, Trade and Industry (METI) is studying financial aid systems and preferential tax systems for encouraging full-scale penetration of solar power generation. A similar aid system and tax system to encourage full-scale penetration of thermoelectric power generation is also considered necessary in the future. However, policies of this type will only be effective after the technical challenges described in the following are overcome, and are not yet required at the present time.

3 Thermoelectric power generating systems

3-1 Mechanism of thermoelectric power generation

Thermoelectric power generating modules comprise two types of elements, a p-type semiconductor element and an n-type semiconductor element. The mechanism of thermoelectric power generation is shown in Figure 4.[1] In the heated n-type semiconductor element (material in which the number of electrons is greater than the number of holes), the electrons in the high temperature region are activated (kinetic energy increases), these electrons are transferred to the low temperature region, generating thermal electromotive force, and the high temperature side reaches a high electrical potential. On the other hand, in the p-type semiconductor element (material in which the number of holes is larger than the number of electrons), the holes in the high temperature region are activated when heated,

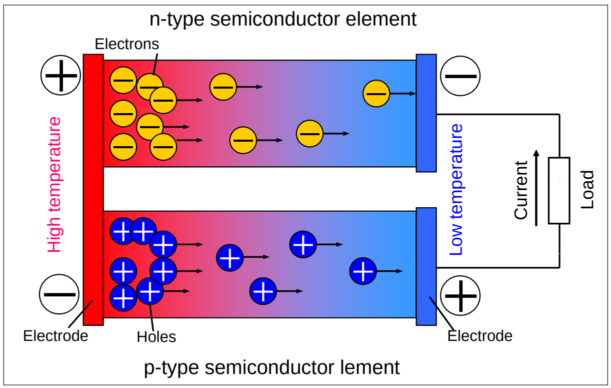

Figure 4 : Mechanism of power generation in thermoelectric power generating module (π-type structure)

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these holes migrate to the low temperature region, generating thermal electromotive force, and the low temperature side achieves a high potential. When these two semiconductor elements are combined, as shown in Figure 4, a current flows between the n-type and p-type semiconductor elements (this phenomenon is termed the Seebeck effect). The power generating performance of thermoelectric conversion materials is expressed by the index Z in the following equation.[6-8]

$ZT = S2\sigma T/\kappa$

where S: Seebeck coefficient (thermal electromotive force per 1K temperature difference, V/K), σ: electrical conductivity (1/(Ω・cm)),κ: thermal conductivity (W/(cm・K)), and T: absolute temperature (K).

The nondimensional power generating performance index ZT is a value obtained by multiplying Z by the absolute temperature and is used as an index of power generating performance. The thermoelectric conversion materials in which the performance index is high, that is, high efficiency materials, are materials in which σ and S are large and κ is small.

The power obtained depends on efficiency, which is determined by the heat flux from the high temperature heat source and the temperature differential during thermoelectric power generation, and the thermoelectric properties of the elements. The maximum efficiency of thermoelectric generating systems is given by Carnot efficiency, which is an index for an ideal heat engine, and the physical properties of the elements, which is termed material efficiency. The relationship between the performance index of a thermoelectric power generating module and the theoretical generating efficiency for the case when Carnot efficiency is 50% is shown in Figure 5.[6] This figure shows that the theoretical generating efficiency approaches Carnot efficiency as the nondimensional generating performance index becomes larger. In the current thermoelectric conversion materials in which ZT ≒ 1, theoretical generating efficiency is approximately 9%.

3-2 Manufacturing process for thermoelectric power generating systems and system efficiency

Thermoelectric power generating systems comprise a high temperature heat source, thermal energy conversion section, and a low temperature heat source, and are made up of a large number of thermoelectric power generating units. Units have a structure in which numerous power generating modules are connected in series, and consist of pairs in which a p-type semiconductor element and electrodes and an n-type semiconductor element and electrodes form the basic structure, as was shown in Figure 4.

Figure 6 shows a schematic diagram of the relationship between the thermoelectric power generating system manufacturing process and generating efficiency, and manufacturing costs. The most effective means of increasing the power generating efficiency of a system is to increase the thermoelectric generating efficiency of the semiconductor material/elements. Because the Seebeck coefficient S, which is one property of thermoelectric generating elements, is small, being on the order of several 100μV/K, the number of thermoelectric generating elements is determined by the output of the generating system, the type of heat source (temperature, temperature differential, thermal flux), and similar factors. Because resistance is smaller than that of ordinary semiconductors, at 10^{-5} to 10^{-4}Ωm, a thermoelectric power generating system takes the form of a high current, low voltage power source (voltage of several 100V or less). The output of the generating system is low voltage and direct current, which means that either a DC-DC converter or a DC-AC converter is required, and it is necessary to respond to the voltage required by the load and to AC load. Normally, auxiliary power such a fan

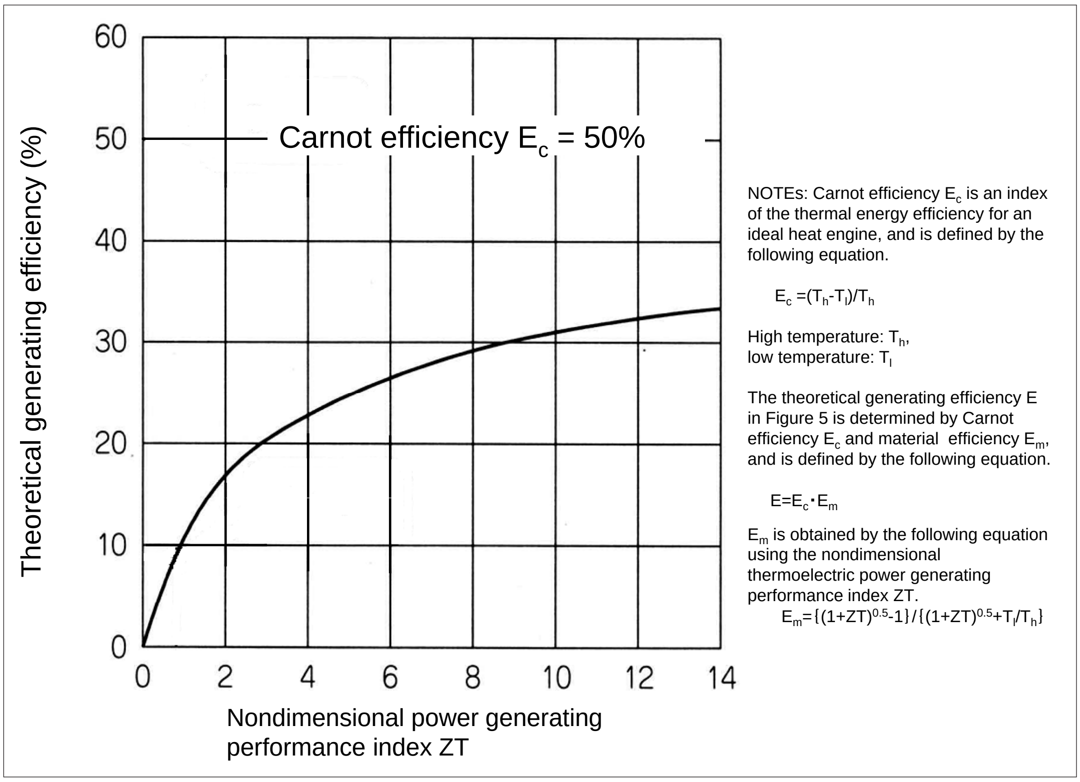

Figure 5 : Relationship between ondimensional power generating performance index of thermoelectric power generating module and theoretical generating efficiency

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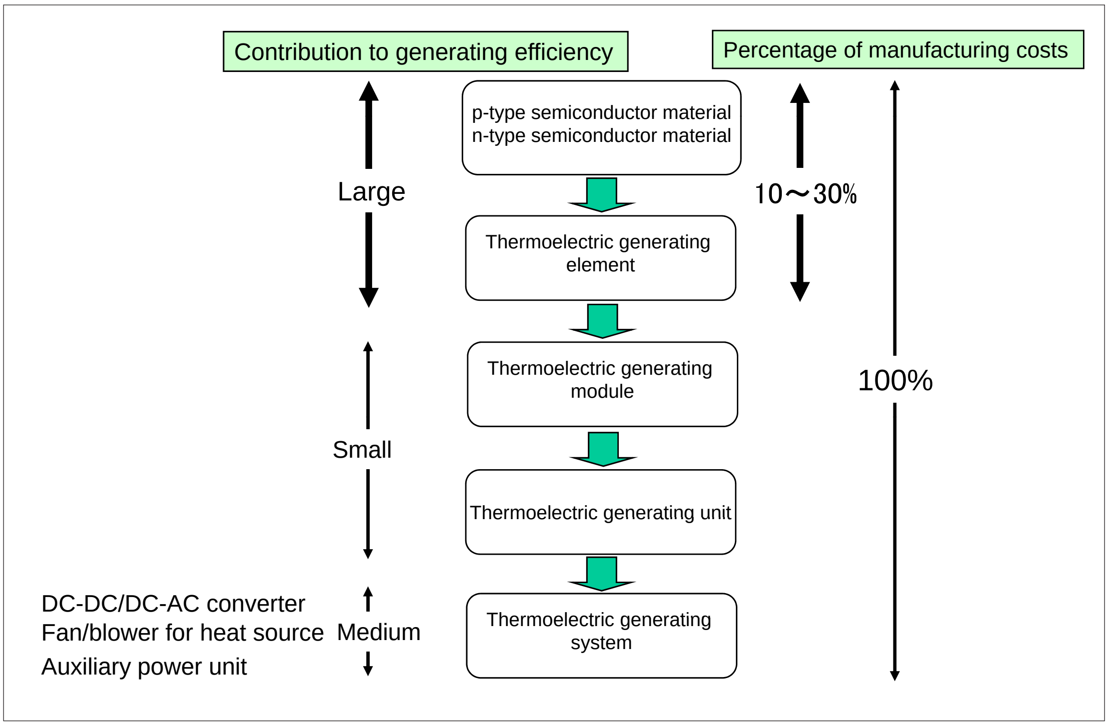

Figure 6 : Schematic diagram on manufacturing process for thermoelectric power generating system and power generating efficiency, and the manufacturing costs

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or blower is used with the high temperature heat source and low temperature heat source in order to pass the heat flow. The output of the generating system is the net output obtained by subtracting these auxiliary power requirements from gross output.[6] As will be discussed in the following, when the temperature generating efficiency of the material/elements is low, it is necessary to increase the efficiency of the total system in the other manufacturing processes.

The largest obstacles to penetration of the present thermoelectric power generation are considered to be economy in the introduction/operation of systems and securing functionality. Therefore, the development of a lower cost system which is convenient to use and offers high reliability is necessary. One conceivable method of achieving this is to use not only as a waste heat energy recovery device, but also as a thermal functional device, for example, as a high speed heat flow control device for effective utilization of thermal energy. Furthermore, in various types of thermal energy systems, higher added value can be achieved in the total system by systematizing waste heat energy recovery devices as high efficiency exergy recovery equipment. For the challenges outlined above, it will be necessary to create a system for smooth competition and cooperation by the R&D organizations of private sector companies, including financial support from the national government.

3-3 Conditions for widespread of thermoelectric power generating systems

Penetration of thermoelectric power generation is considered possible if system efficiency exceeding 10% can be realized. Therefore, a material which satisfies a nondimensional power generating performance index of ZT>2 is necessary. Element efficiency of 15% or higher and output density of $1W/cm^2$ or higher are considered to be conditions for achieving this.[6]

The fields in which thermoelectric power generating technology should be applied will depend on the temperature level and form of the heat source used. Various fields exist, including application to large-scale systems for the purposes of energy saving and environmental protection, consumer products oriented to small-scale power

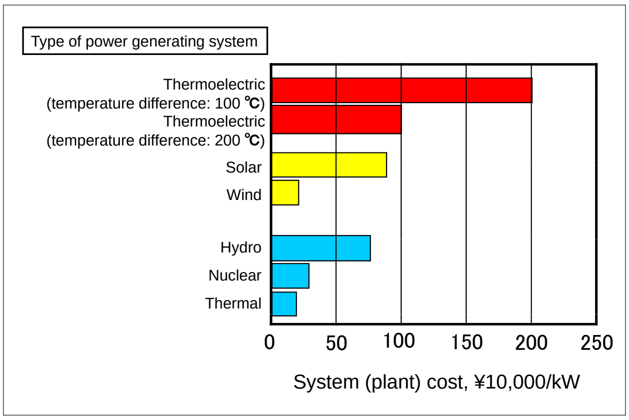

Figure 7 : Cost of various types of power generating systems (plants)

Prepared by the STFC based on Reference[9-12]

sources, etc. In practical application of these systems and equipment, it is important to secure economy, in other works, the cost of the power generating system and its performance. Figure 7 shows the system (plant) cost per unit of output in various types of power generating systems. If the cost of thermoelectric power generating modules can be reduced to the level of the current solar power generating systems, a broad expansion in the fields of application is conceivable. The system cost of the current solar power systems has been reduced to around \800/W.[9-12] Accordingly, the cost of the current thermoelectric power generating systems is approximately 1.3 to 2.5 times that of solar power generating systems.

4 Thermoelectric conversion materials and power generating performance

4-1 Thermoelectric conversion materials to date

As described in section 3-3, the ideal thermoelectric conversion material is a material with a nondimensional power generating performance index ZT of 2 or higher. Figure 8 shows the history of the development of the main thermoelectric conversion materials from the viewpoint of ZT. To date, the main materials have been intermetallic compounds such as bismuth telluride (Bi_2Te_3), lead telluride (PtTe), zinc antimonide (ZnSb), SiGe, iron silicide ($FeSi_2$), etc. Among these, in particular, Bi_2Te_3 based compounds have a large ZT in the comparatively low temperature region from room temperature up

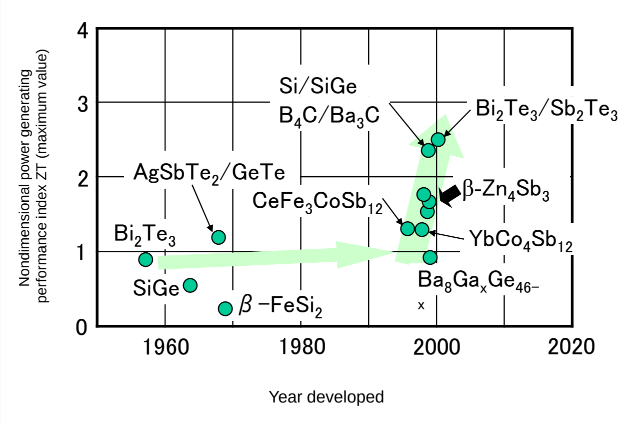

Figure 8 : History on development of main thermoelectric conversion materials from viewpoint of nondimensional power generating performance index

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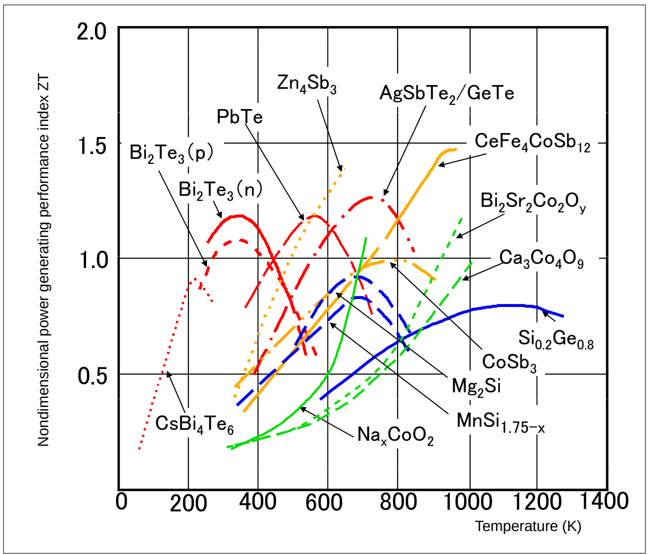

Figure 9 : Temperature dependency on nondimensional power generating performance index of main thermoelectric conversion materials

Prepared by the STFC based on Reference[6,13]

to approximately 450K, and are the most widely used thermoelectric conversion material at present.

Figure 9 shows the temperature dependency of the ZT of thermoelectric conversion materials.[6,13] The ZT of the respective materials tends to increase with temperature and then decrease after reaching a peak. The power generating performance of Bi_2Te_3 and Zn_4Sb_3 is ZT=1.0-1.25 in the low/medium temperature region of 300-700K, while a compound of $AgSbTe_2$/GeTe (composition ratio 1:1) shows ZT ≒ 1.2 at 700K and $Si_{0.2}Ge_{0.8}$ shows ZT ≒ 0.7 at approximately 1100K. In the temperature region under 500K, BiTe based compounds display high ZT. In the medium temperature region of 700-900K, $AgSbTe_2$/GeTe and $CeFe_4CoSb_{12}$ are high ZT thermoelectric conversion materials, and in the high temperature region above 900K, the high ZT materials are $Si_{0.2}Ge_{0.8}$, $Bi_2Sr_2Co_2O_y$, and $Ca_3Co_4O_9$.

With materials which were suitable for practical application, during the last 50 years, it was extremely difficult to increase performance to ZT>1 because electric resistance and thermal conductivity, which are parameters of ZT, display a property of mutual dependence. Recently, however, materials having performance of ZT>2 have been reported in several papers. There are also examples of research in which ZT>1 could be obtained in thermoelectric conversion materials by nanostructuring, even with the same material. However, with these materials (Bi, Te, Pb, Sb, and Ag based materials, etc.), no manufacturing processes have been developed for upscaling to the size of modules suitable for practical use.

4-2 Low environmental impact thermoelectric conversion materials with secure resource supplies

As shown in Figures 8 and 9, the thermoelectric conversion materials which have been used up to the present time are intermetallic compounds of Bi, Sb, Pb, and other heavy metals, and consist of elements with limited global reserves. It is also thought that full-scale practical application of these materials will be difficult in the future from the viewpoint of environmental impact. Recently, metal oxides have attracted attention, as these are materials which are familiar, exist in abundance, have low environmental impact, and also have high heat resistance. However, in comparison with the heavy metal materials, the thermoelectric power generating efficiency of these oxides is low.[6,14,15]

Figure 10 shows a schematic illustration of the main thermoelectric conversion materials researched to date and materials that should be priority objects of R&D in the future. Priority should be placed on R&D of silicide-based and metal oxide-based materials, as abundant reserves of raw material resources exit, systems can be composed at low cost, and these substances have low environmental impacts. With magnesium silicide (Mg_2Si), low generating efficiency is a problem, but it is thought that the efficiency of the module as a whole can be increased by innovations in the electrical circuit, etc.

Silicide-based compounds such as Mg_2Si, β-$FeSi_2$, $MnSi_{1.73}$, etc. will be promising candidate with low environmental impacts in the future. Although improvement of performance has been studied previously from the viewpoints of material microstructure and processes, performance is low, at ZT ≒ 0.2 (by element efficiency, 2-5%). However, element efficiency of 6.4% has reportedly been achieved with a module using a combination of microstructure-controlled $MnSi_{1.73}$ (p-type semiconductor) and Mg_2Si (n-type semiconductor).[6,15]

The process used to synthesize ceramics, which are metal oxides, from an aqueous solution at normal temperature and normal pressure is a manufacturing method which is suited to low cost mass-production, and the environmental impact of the materials themselves is small. In high efficiency thermoelectric conversion materials which operate at high temperatures, it would seem that metal oxides will become central, considering their high-temperature stability as substances and other advantages.[6,15]

$CeFe_3CoSb_{12}$ is a p-type semiconductor which is called a Skutterudite compound and has an unusually large value of hole mobility of 2000-8000cm2/Vs at room temperature due to the unique band structure and electronic structure of the compound. Performance of ZT ≒ 1.3 (800K) has been realized with this substance by reducing its thermal conductivity to approximately 1/5 that of $CoSb_3$.[6,15]

A semiconductor material which possesses low thermal conductivity on the level of amorphous materials and high electron mobility on the level of crystals is the clathrate compound Ba_8Si_{46}. Here, the term "clathrate compound" refers to compounds in which small molecules are contained in spaces created by the crystal lattice and exist as stable substances without depending on a covalent bond. These materials have a complex cage structure, and lattice thermal conductivity is small, being on the order of amorphous α-Ge and quartz glass (α-SiO_2), due to phonon scattering of the atoms in the cage. At present, power generating performance is ZT ≒ 0.6 (900K), but ZT ≒ 1.5 is expected to be possible by optimization of the carrier (electron, hole) concentration and element substitution.[6,15]

Other thermoelectric conversion materials include Zn_4Sb_3, which is a zinc antimony-based substance, strongly correlated electron system compounds, superlattice compounds, and $NaCO_2O_4$ and other

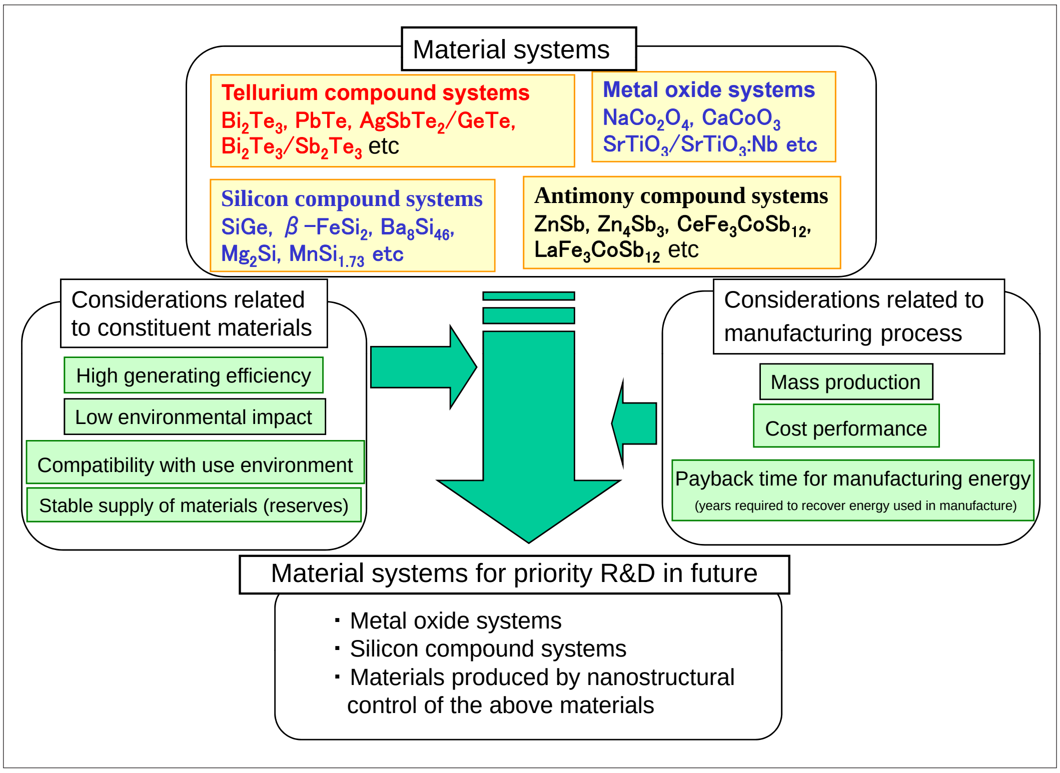

Figure 10 : Main thermoelectric conversion materials researched to date and material systems for priority R&D in the future

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metal oxides. Results exceeding ZT=1 have also been reported with needle-shaped single crystal $CaCoO_3$.

4-3 Trends in R&D on thermoelectric conversion materials in foreign countries

In the United States, research and development on thermoelectric power generating technologies is being promoted with the priority narrowed to the waste heat energy of automotive exhaust gas in the FCVT (Freedom Car & Vehicle Technologies) Program, which is part of the Energy Efficiency and Renewable Energy Project of the U.S. Department of Energy (DOE). Vigorous development is underway, including R&D extending to the nanostructured materials technology region, as represented by superlattice materials and their applied technologies.[16-18]

In the past, only a small amount of research and development in connection with thermoelectric power generating technologies had been carried out in Europe, but recently, R&D in this field has continued to be active, centering on Germany. The Fraunhofer Gesellschaft (FHG) research organization is conducting research and development centering on applied technologies for industry in Germany and other countries, but among the 56 FHG laboratories in Germany, the Institute for Manufacturing Technology and Applied Materials Research (IFAM), in cooperation with the Institute for Physical Measurement Techniques (IPM) and the Institute for Integrated Circuits (IIS), is carrying out R&D related to nanoscale thermoelectric conversion material processes and the practical applicability of energy supply modules and systems.[19] On the other hand, the Deutsches Zentrum fur Luft- und Raumfahrt (DLR), which is a German aerospace research center, is engaged in R&D activities in connection with planning of the use of thermoelectric power generating sensors in space and the creation of international standards for thermoelectric power generating performance evaluation techniques.[20]

5 Innovative thermoelectric conversion materials by nanostructural control

The development of thermoelectric conversion materials with dramatically higher efficiency is considered possible using nanostructural control techniques, etc. If it is possible to achieve a level at which these material technologies can be applied to modules and systems that are competitive in terms of cost performance, a large expansion of the energy saving/low environmental impact technology industry is expected, with thermal functional devices, thermal energy recovery devices, etc. as its objects.

Among the material systems shown in Figure 10, Table 1 shows examples of innovative thermoelectric conversion materials by nanostructural control, which is considered to be an important area for promotion of R&D in the future. Figure 11 is a schematic diagram of the main measures related to nanostructural control for improving power generating performance, with the main thermoelectric conversion materials arranged from the viewpoint of the energy gap, thermal conductivity (lattice composition), and carrier (electron, hole) mobility of the thermoelectric conversion materials, these being the factors which control performance. The following presents an outline of examples of research in these respective areas.

5-1 Thermoelectric conversion materials with nano thin film structure

The following are examples of research aimed at realizing high efficiency thermoelectric conversion materials by structural control at the nano level using only abundant elements, without use of scarce elements.

The fact that $SrTiO_3$, which is an insulator, becomes a thermoelectric conversion material in the high temperature region (approximately 750 °C) when a small amount of Nb is added has attracted attention. Because its power generating efficiency is low, at less than one-third that of the heavy metal-based materials, a method of accumulating electrons in an extremely thin film sheet with a thickness of several nm has been proposed as a method of increasing its thermal electromotive force. Conversely, because it is difficult to accumulate electrons in heavy metals, as these substances pass electricity readily, it is difficult to increase the power generating efficiency of the heavy metal materials by this method. However, it is possible to store electrons by using an insulator. By creating a sandwich structure ($SrTiO_3/SrTiO_3$: $Nb/SrTiO_3$), comprising an $SrTiO_3$ thin film sheet with a thickness of 0.4nm, in which electrons are formed by addition of Nb, between upper and lower sheets of non-Nb-added $SrTiO_3$,which is an insulator, the thermoelectric power generating efficiency of this composite thin film was successfully increased to approximately double that of the conventional heavy metal-based material.[21,22]

If it is possible to develop a manufacturing process that is not limited to the small area, thin film level, but can expand this type of nano thin film structure thermoelectric conversion material to large area films and bulk materials consisting of nanostructures, this will open the way to application to practical systems.

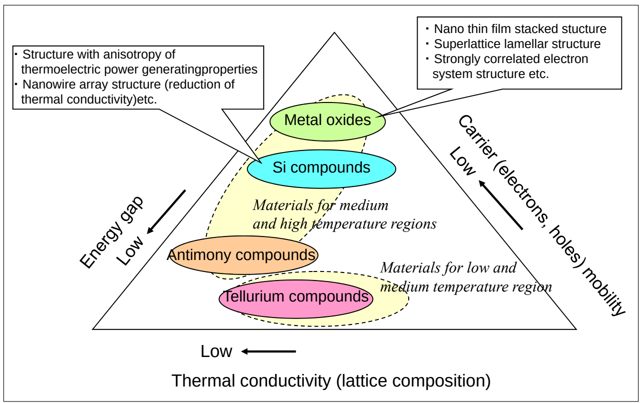

Figure 11 : Schematic diagram on factors controlling performance in main thermoelectric conversion materials systems and measures for improvement of power generating efficiency from viewpoint of structural control

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5-2 Superlattice compound thermoelectric conversion materials

This is a concept which attempts to achieve high thermoelectric power generating efficiency by independently controlling electrical conductivity and thermal conductivity in different nanoblocks. An attempt to realize high thermoelectric power generating efficiency in hybrid crystals consisting of a regular periodic arrangement of lamellar-structured oxides, and particularly, two or more different symmetrical sub-lattices has been announced. This is an attempt to create a high efficiency thermoelectric conversion material by constructing a low-dimensional, anisotropic structure by combining multiple types of nanoblocks having a thermoelectric function. Theoretical calculations in connection with low-dimensional crystal structures have

Table 1 : Examples of research and development on thermoelectric conversion materials by nanostructural control

Class	Example of materials being studied	Concrete technique or research results
Nano thin film structure	$SrTiO_3/SrTiO_3$:$Nb/SrTiO_3$	・Sandwich structure in which an Nb-added $SrTiO_3$ thin film sheet (thickness: 0.4nm) is put between upper and lower insulators of $SrTiO_3$.
Superlattice compound	Bi_2Te_3/Sb_2Te_3	・Construction of low-dimensional anisotropic structure by combining multiple nanoblocks having a thermoelectric function. ・Possibility to realize ZT ≒ 2.4(room temperature) by thin film elements with by superlattice structure (quantum well, quantum wire, quantum dot) .
Nanowire array	Si nanowire array	・Electrochemical synthesis of large area array of Si nanowires (diameter; 20-300nm). The thermal conductivity of Si nanowires with diameter of approximately 50nm was reduced to 1/100 (ZT=0.6).
Strongly correlated electron system	$NaCo_2O_4$ $(Ce_{1-x}La_x)\ Ni_2$ $(Ce_{1-x}La_x)\ In_3$ $CeInCu_2$	・Confirmed that lamellar oxide $NaCo_2O_4$ has a large thermal electromotive force of 100μV/K (at room temperature) and large electrical conductivity of $5x10^3/(\Omega \cdot cm)$.
Plane structured element	$Na_xV_2O_5$ V_2O_5	・Power generation using only an n-type semiconductor elements (an abundant variety of n-type semiconductors are available) by producing a temperature gradient between the two sides of the element plane and obtaining an electron flow within the plane. ・Thin film, compact size, and high density are possible in thermoelectric elements, as in conventional semiconductors thin film devices.

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also indicated the possibility that thermoelectric power generating efficiency can be dramatically increased by superlattice structures such as quantum wells, quantum wires, quantum dots, and the like. In addition, Z ≒ T2.4 (room temperature) was reportedly obtained with a Bi_2Te_3/Sb_2Te_3 superlattice thin film element.[6,15]

5-3 Nanowire array thermoelectric conversion materials

This is an example of research in which a non-dimensional power generating performance index of ZT=0.6 at room temperature was obtained by reducing the thermal conductivity of Si nanowires with a diameter of approximately 50nm to 1/100 that of bulk Si when a large area array of wafers, in which a large number of coarse Si nanowires with diameters of 20-300nm were arranged, was synthesized electrochemically. Because the thermal conductivity of nanowires should be near that of the limit value of amorphous Si, the behavior of the nanowires in this report cannot be explained by the existing theory. The thermoelectric power generating property of bulk Si is inferior to that of conventional thermoelectric conversion materials. If it can be assumed hypothetically that a large reduction in thermal conductivity can be achieved with virtually no effect on the Seebeck coefficient or electrical conductivity, then Si nanowire arrays are promising as high performance thermoelectric conversion materials.[23-25]

Large-scale processing of Si is possible, but because the electrical and thermal conductivity of htis substance are high, its thermoelectric power generating property is low. However, from the viewpoint of resource supplies and low environmental impact, assuming the ZT value of Si nanowires can be improved by approximately 100 times that of bulk Si over a wide temperature range by optimizing the dimensions of the nanowires and amount of impurity doping, this would be an extremely significant achievement which would heighten the potential for industrial application. If it is possible to establish a method of structuring Si in nanowire arrays and closely controlling the shape of the nanowires and the amount of impurity doping, Si nanowires will have great potential as high efficiency thermoelectric conversion materials. This research will also attract attention from the viewpoint of use of a material with a stable supply and low environmental impact, and from the viewpoint of cost performance.

5-4 Thermoelectric conversion materials with strongly correlated electron system

The term "strongly correlated electron system" indicates a system in which the effective Coulomb interaction between pairs of electrons in a substance is strong. Many substances with strong electron correlation exist in systems including transition metals and rare earth metals (REM). As strongly correlated compounds in which attention has focused on the f-electrons in REM, $(Ce_{1-x}La_x)Ni_2$, $(Ce_{1-x}La_x)In_3$, $CePd_3$, $CeInCu_2$, etc. have attracted interest as materials with high thermoelectric power generating performance in the temperature region below room temperature.[6,15]

It has been found that $NaCo_2O_4$, which is a lamellar oxide, has a large thermal electromotive force of 100μV/K and large electrical resistance of $5x10^3$ (Ω・cm) at room temperature. This lamellar oxide system has a large thermal electromotive force of 100μV/k irrespective of the fact that it also has a high carrier concentration of 1021-1022cm^{-3}. The cause of this phenomenon has been explained by the fact that the strong electron correlation in the crystal plays an important role.[6,15]

On the other hand, although it had conventionally been thought that metals with high electrical conductivity have low thermoelectric power generating efficiency, a large thermoelectric power generating effect was discovered in a cobalt oxide ($CaCoO_3$) in Japan in 2000. At present, it is thought that guidelines for searching for higher efficiency thermoelectric conversion materials can be obtained by elucidating the mechanism responsible for the manifestation of the large thermoelectric power generating effect in this substance. [6,15]

5-5 Thermoelectric power generating elements with plane structure

To date, as shown in Figure 4, thermoelectric power generating elements have comprised thick pn junctions which utilize the temperature gradient in the thickness direction of the element, and materials having both p-type and n-type electrical conduction characteristics are necessary. Because virtually all of the abundant types of metal oxides are n-type, and metal oxides having both p-type and n-type electrical conduction characteristics are rare, the realization of conventional type of pn junction thermoelectric power generating element structure with only metal oxides had been considered difficult.

In plane-structured thermoelectric power generating elements, ,power is generated using only an n-type semiconductor element by producing a temperature gradient between the two sides of the element plane and obtaining an electron flow within the plane. If this structure and principle are used, it is expected to be possible to produce thermoelectric power generating elements with a thin film structure, compact size, and high density, like those in conventional semiconductor thin film devices, in plane-structured thermoelectric power generating element.[26,27]

6 Current status of R&D projects on thermoelectric power generating technology in Japan

This region was mentioned as part of the target of "Materials technologies to realize use of unused energy," which is a priority R&D theme in the Materials region in the Nanotech & Materials field in Promotion Strategies by Field in Japan's Third Science and Technology Basic Plan.[28] Subsequently, this was reviewed based on the "Cool Earth – Innovative Energy Technology Program" (established March 2008), and was taken up in the "Technology Strategy Map 2008" of the Ministry of Economy, Trade and Industry (METI) as "Unused micro-energy power conversion." However, it is not included in the individual technologies that are expected to make a large contribution to the policy goal of "Improvement of total energy efficiency" (Figure 12).[29] As mentioned in section 2-1, the thermal energy discarded from energy systems of all types is not negligible.

In the Nanotechnology Field of the above-mentioned "Technology Strategy Map," the fields of Environment and Energy, Electronics and Communications, and certain others are set as important exit fields for nanotechnology. A map was established to provide an overview of technologies from the viewpoint of how nanotechnology can contribute to realizing the functions demanded by the respective technical regions in these fields. Figure 13 shows a summary of the technical issues related to the Waste Heat Power Generating Technology region in this technology map. Waste heat power generating technology was selected as an important technology in waste heat utilization technologies in the Electronics, Information, and Semiconductor region, and is shown in the technology roadmap together with the issues for development in that year.[29,30]

The report by the New Energy and Industrial Technology Organization (NEDO) on achievements in connection with thermoelectric power generating technologies published to date mentions 115 items.[31] However, much of this research and development is work carried out as Grant for Industrial Technology Research Projects, which are budgeted on a one-year basis. In popularizing thermoelectric power generating technologies in effective recovery of unused waste heat energy, the timing for achieving high efficiency and low cost in materials/modules, development of low environmental impact thermoelectric conversion materials, and achievement of 15-20% module power generating efficiency shown in Figure 13 should be moved up (to before 2020). For this, as will be discussed in Chapter 7, it will be necessary to strengthen the R&D promotion system, narrow the focus of the object thermoelectric conversion materials, and invest R&D funds on a priority basis.

Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT) has positioned research and development of "Innovative technologies for substitute materials for scarce and inadequate resources which will be decisive for solving resource problems" in the "Strategic Prioritized S&T" enumerated in the "Nanotech/ Materials" field, which is one of the four "Priority fields to be promoted" in the "Third Science and Technology Basic Plan," and began its "Element Strategy Project" in FY2007. Thermoelectric conversion materials were taken up as one assumed research topic in the public invitation to submit project proposals in FY2008, and scientific elucidation of the role of the elements which make up those materials and the mechanisms by which their functions are manifested are mentioned (Figure 14).[32,33]

7 Future approaches to R&D on thermoelectric conversion materials

As future approaches to research and development in connection with thermoelectric conversion materials, the following should be considered.

(1) In Japan, which is a resource-poor nation, efforts to construct a next-generation energy utilization society by development, introduction, and penetration of innovative energy technologies are indispensable. While the government continues to indicate the directions for future technologies over the long term, it should also promote research and development through prioritized investment, particularly in the case of materials systems which involve high risk and hurdles. R&D in connection with thermoelectric conversion materials falls under this category.

(2) If it is possible to develop modules and systems with high cost performance by utilizing thermoelectric conversion materials, a large expansion in the energy saving/low environmental impact technology industry can be expected, with objects including thermal functional devices, heat recovery devices, etc. In the future, Japan should take a position of world leadership in this field and secure its technical superiority over other countries.

(3) As an approach to promoting future R&D projects, the roadmap from R&D of fundamental and basic technologies to practical application and the issues which require prioritized efforts should be clarified, and concrete measures which promote R&D in connection with materials technologies, device technologies, and applied technologies in

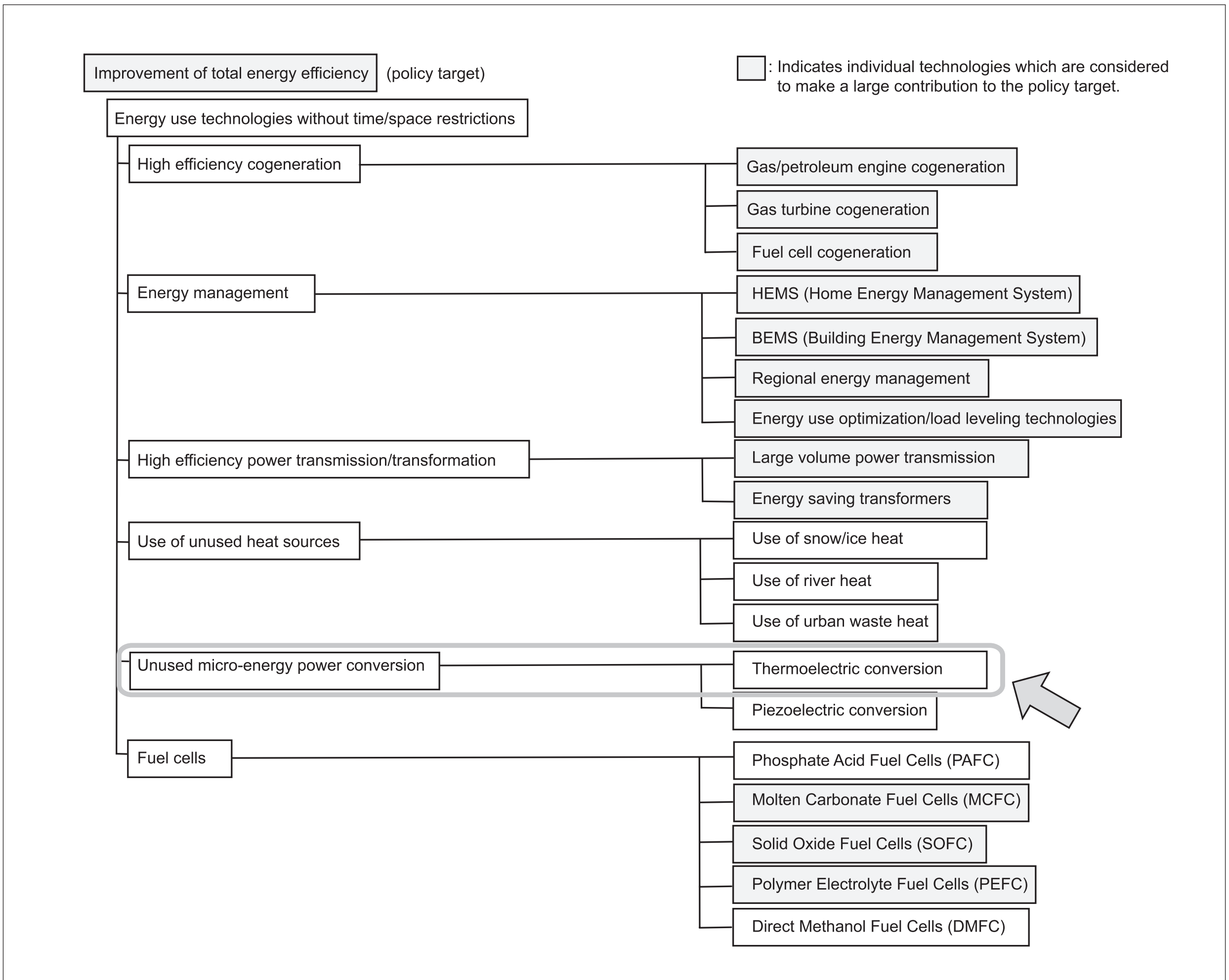

Figure 12 :Technologies for “Unused micro-energy power conversion” in technologies contributing to “Energy field – Improvement of total energy efficiency” in METI Technology Strategy Map

Prepared by the STFCbased on Reference[29] parallel should be taken, based on a division of short-term and long-term issues.

(4) As a long-term issue, development of new materials with revolutionary power generating efficiency and R&D on thermoelectric power generating devices using these materials should be promoted. As materials technologies, it is desirable to study novel nanomaterials systems based on superlattice and quantum structures (quantum wells, fine wires, dots) using nanostructural control and related manufacturing processes, metal oxides with low environmental impacts, etc. In parallel with this, it is also desirable to promote high efficiency, downsizing, and operability in a wide temperature range in power generating module technologies.

(5) In projects promoted by the government, clarification of priorities when implementing research and development of new thermoelectric conversion materials is demanded, based on a total scenario from fundamental and basic development to practical application or expanded penetration.

8 Conclusion

In the realization of a low carbon society, reductions in unused waste heat and various energy systems will be necessary. For this, popularization of thermoelectric power generating system will be indispensable. At present, thermoelectric power generating systems have been applied practically in limited fields, but the materials used in these systems have the problem of unstable supplies of resources, and because their main components are heavy metals, high environmental loads are a concern. Moreover, the current systems are also inferior economically due to the low power generating efficiency of the elements. For these reasons, full-scale penetration of thermoelectric power generating systems has not progressed, even though the history of technical development has now reached the half-century mark.

The highest priority for solving the problems associated with these thermoelectric power generating materials is considered to be research and development of thermoelectric conversion materials which offer high efficiency, stability in the use environment, and low cost. The use

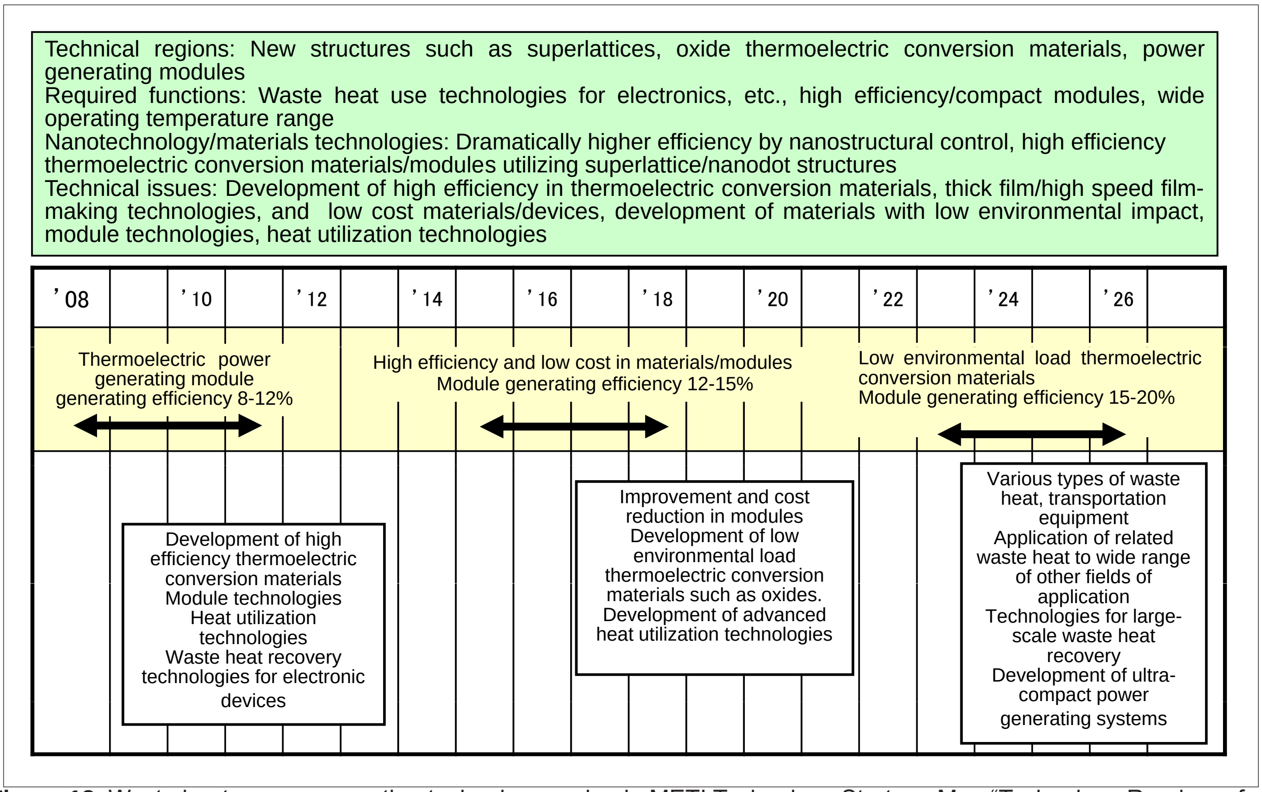

Figure 13 :Waste heat power generation technology region in METI Technology Strategy Map "Technology Roadmap for Nanotechnology Field – Electronics, Information, and Semiconductors"

Prepared by the STFCbased on Reference[29]

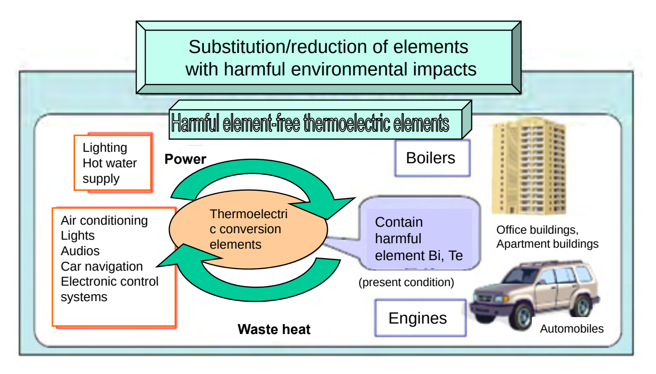

Figure 14 Examples of issues for research in MEXT "Element Strategy for Solving Resource, Environmental, and Energy Problems"

Source : Reference[33]

of materials with secure resource supplies and low environmental loads is also indispensable. Therefore, future research and development should shift to metal oxides and silicon compounds. In particular, attention will focus on nano thin film structures, superlattices, nanowire arrays, strongly correlated electron system compounds, etc. of these substances as objects of research and development.

In view of the importance of the ripple effect on the realization of a low carbon society, etc., as a future approach to R&D on thermoelectric power generating technologies, R&D projects based on scenarios which further clarify the roadmap from R&D of fundamental and basic technologies to practical application and the issues that require prioritized efforts should be divided into short-term and long-term issues, and materials technologies, device technologies, and applied technologies should be promoted in parallel. In particular, R&D on nanostructural control of metal oxides, etc. and their manufacturing processes is a long-term challenge, but because the technical hurdles are high, projects promoted under government leadership are demanded. If it is possible to discover revolutionary thermoelectric power generating elements with power generating efficiency of 20% or higher by using innovative materials, and to develop modules and systems with high cost performance, the ripple effect on the energy saving/low environmental impact technology industry will be immeasurably large.

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